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ORIGINAL ARTICLE

Point source pollution and variability of nitrate concentrations in water from shallow aquifers

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Abstract Agriculture is one of the several major sources of nitrate pollution, and therefore the EU Nitrate Directive, designed to decrease pollution, has been implemented. Point sources like septic systems and broken sewage systems also contribute to water pollution. Pollution of groundwater by nitrate from 19 shallow wells was studied in a typical agricultural region, middle Podravina, in northwest Croatia. The concentration of nitrate ranged from <0.1 to 367 mg/l in water from wells, and 29.8 % of 253 total samples were above maximum acceptable value of 50 mg/l (MAV). Among regions R1–R6, there was no statistically significant difference in nitrate concentrations ($F = 1.98$; $p = 0.15$) during the years 2002–2007. Average concentrations of nitrate in all 19 wells for all the analyzed years were between recommended limit value of 25 mg/l (RLV) and MAV except in 2002 (concentration was under RLV). The results of the repeated measures ANOVA showed statistically significant differences between the wells at the point source distance (proximity) of <10 m, compared to the wells at the point source distance of >20 m ($F = 10.6$; $p < 0.001$). Average annual concentrations of nitrate during the years studied are not statistically different, but interaction between proximity and years is statistically significant ($F = 2.07$; $p = 0.04$). Results of k-means clustering confirmed division into four clusters according to the pollution. Principal component analysis showed that there is only one significant factor, proximity, which explains 91.6 % of the total variability of nitrate. Differences in water quality were found as a result of different environmental factors. These results will contribute to the implementation of the Nitrate Directive in Croatia and the EU.

Keywords Nitrate · Pollution · Point source · Water · Shallow well · Croatia

Introduction

The most important and abundant source of drinking water in the European Union (EU) is groundwater constituting over 80 % of the supply (Council Directive 2000). Pollution of groundwater is caused by different pollutants, among which nitrate plays the most important role. Nitrate pollution from agriculture is an issue of major concern for the UN (Addiscott et al. 1991), and a series of environmental policies have been implemented in the EU to decrease nitrogen (N) emissions from agriculture. The Nitrate Directive is one of the main policies to reduce nitrate leaching from agriculture primarily through good agricultural practise and the application of organic and mineral fertilizers according to regulations (Velthof et al. 2014).

As nitrogen is the key factor in a high and stable cultivated plant production, it is no surprise that modern agriculture affects nitrogen content in water, as it is a high nitrogen user (Addiscott et al. 1991; Bašić and Herceg 2010). Nitrate concentration in natural waters has been increasing during the last few decades, coinciding with the

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increased use of mineral fertilizers and a higher yield of cultivated plants in agriculture. This problem has become even more significant by introducing the stricter standards concerning the nitrate content of drinking water in the EU. The maximum acceptable value (MAV) is 50 mg/l NO_3^- (Regulation 2013), but the recommended limit value (RLV) is only 25 mg/l NO_3^- (Council Directive 1991).

Agriculture is the biggest source of pollution because of the so-called diffuse source pollution that does not originate from a single discrete source. Pollution is often a cumulative effect of small amounts of contaminants gathered from a large area (US EPA 1987). Numerous scientists have shown nitrate leaching from agricultural areas. Elhatip et al. (2003) showed that agricultural activities contribute to an increased nitrate concentration in groundwater either directly by nitrate leaching from agrochemicals or by agrochemicals that affect the processes in the soil and increase nitrate leaching from the soil. Nitrate leaching depends on a variety of environmental factors. Mild climate and favorable winter temperatures allow the extension of the growing season of plants, which reduces nitrate leaching (Hooker et al. 2008). Benson et al. (2006) also evaluated the importance of the excessive use of agrochemicals. They point out that the use of fertilizers in doses of 500 kg/ha increases the nitrate concentration in the water up to a distance of 2 km from the well.

Point source pollution refers to contaminants that enter a waterway from a single, identifiable source such as livestock farms, slurry lagoons or manure depots with an inappropriate building or location (US EPA 1987). Dense populations and discharges from point sources like septic systems or broken sewer systems contribute significantly to water pollution by nitrate in urban and suburban areas (Nemčić-Jurec et al. 2007, 2013; Drake and Bauder 2005; Melian et al. 1999; US EPA 1987).

Effects of point sources of pollution are usually localized and limited (Krapac et al. 2002; Nemčić-Jurec et al. 2013). Ciravolo et al. (1979) showed that point source (lagoon with liquid pig manure) affected the concentration of nitrate in the water at the distance of 36 meters from the well. However, they point out that the contamination occurred in the wells located on sandy soil, while at locations where there is clay soil, there was no significant pollution. In similar studies, Richards et al. (1996) showed that the concentration of nitrate in the water from the well in sandy soil, at the distance of 6 m from the point source pollution (animal feedlot or barnyard), was twice as high (3.6 mg/l) compared to the concentration of nitrate (1.8 mg/l) from the wells located 60 m from the pollution. Nemčić-Jurec et al. (2013) showed by comparison of nitrate concentration in two different geological areas that the nitrate concentration occasionally or regularly exceeds MAV in wells close to point sources of pollution (within 10 m of the well). In both areas of research, however, the frequency of unsafe samples was significantly higher in Prigorje area compared to Podravina area. Nitrate concentration in water depends on the vertical and horizontal transports of nitrate leaching (Houben et al. 2001). They point out that the highest nitrate concentrations are determined in the shallow aquifers that are richer in oxygen at a depth of 12 m. Katz et al. (2004) showed that the concentration of nitrate in the shallow aquifer is spatially and vertically highly variable. Although the average nitrate content between the shallow and deep zone was not significantly different (0.13 and 0.17 mg NO_3-N/l), the maximum content was much higher in the shallow zone (7.3 mg NO_3-N/l) compared to the deeper zone (1.6 mg NO_3-N/l). The variability of nitrate concentration was higher in shallower layers.

Podravina is an area of relatively intensive agriculture where, according to modern agricultural demands, higher doses of organic and mineral fertilizers are applied, causing leaching of the soil and nitrate input in aquatic ecosystems. Considering the large share of arable land in the River Drava basin, the highest possible nitrate pollution of water in this region can be expected. Due to the increasing trend of application of mineral and organic fertilizers in the world (Woo-Jung et al. 2007; Pacheco et al. 2001; Bouwman et al. 2005; Cetindag 2005; Widory et al. 2003) and, on the other hand, due to stricter criteria concerning reduction in nitrate pollutions in water (EU Nitrate Council Directive 1991), the aim of this research was to investigate the annual nitrate concentration variability in the area of an intensive agriculture and dense population of the middle Podravina region. The areas especially prone to pollution are easily permeable soils in drinking water protection zones in shallow unconfined aquifers (Burkart and Stoner 2007; Kraft and Stites 2003). Therefore, the aim was to determine to what extent point sources of pollution from agriculture and septic systems contribute to total pollution, as well as to determine the nitrate concentration variability in individual wells depending on the environmental factors.

Study areas

Location

The locations of the wells within the regions (R1–R6) are illustrated in Fig. 1. The regions are based and defined on political (municipality) and geographical boundaries. The study area (20 × 30 km) located in the water catchment of middle Podravina in northwest Croatia extends from Legrad in the east to Sokolovac in the west. From the north, the area is bordered by the state border with the Republic of Hungary and in the south with the northern slopes of Bilogora and Papuk. The old alluvial terraces area is

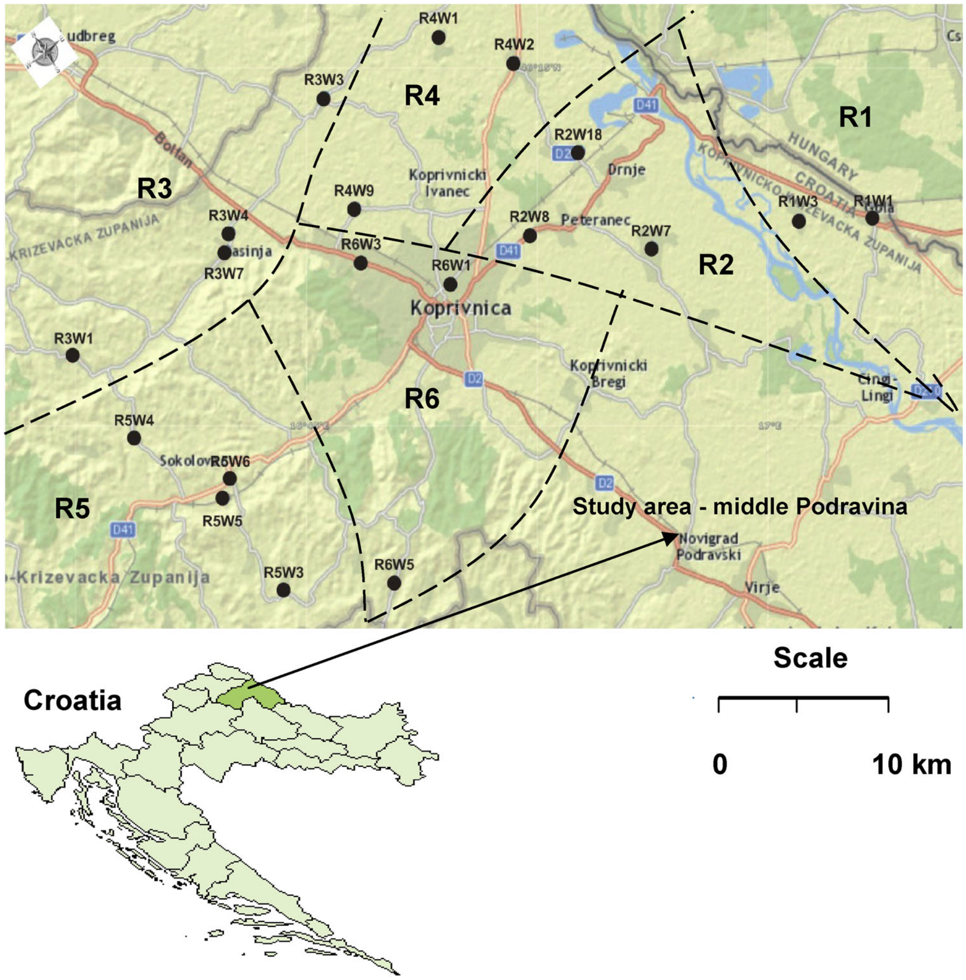

Fig. 1 Locations of the wells within the regions in middle Podravina (*R* region, *W* well)

composed of drift of the River Drava and its tributaries, as well as terraced sediment.

Climate and hydrogeology

From the hydrogeological point of view, the quaternary sand–gravel aquifer is the most important. The top part of the aquifer is built of sand and clay, with a significant proportion of quicksand and mostly of swampy loess in the southern and eastern part of water catchment (Mayer et al. 1996). A mild-continental climate dominates, and the average annual precipitation is about 820 mm. The average annual temperature is about 11 °C which indicates mild-warm climate (data obtained from the Metrological and Hydrological Service). These climate conditions favor agricultural production and increased population density.

Land use and point sources of pollution

The research area is inhabited by about 60,000 people with traditionally developed plant and animal production. The total research area covers 177,464 ha, out of which agricultural land covers 59 %. The remaining area consists of forests (32 %), arid land, settlements and water surfaces (9 %). Of the agricultural land, 99 % is arable (gardens, orchards, vineyards and meadows) and 1 % is pastures.

According to the data of the Faculty of Agriculture, average doses of organic and mineral fertilizers applied in middle Podravina (152 kg N/ha agricultural area) are higher in comparison with the average doses of fertilizers applied in Croatia (54 kg N/ha agricultural area). In the research area, point sources of pollution of agricultural origin such as farms and barns, and landfill of organic fertilizers depots are often very close to the wells (5–20 m). Most of the population in urban areas, up to 80 %, is connected to a sewerage system, while the population of suburban areas use septic systems which are also often very close to the wells.

On the sandstone outcrop area, the soil is freely draining so the nitrate input from point sources of pollution can be expected to accumulate in the aquatic ecosystems including the River Drava basin.

Materials and methods

Sampling

Nitrate concentration variability was tested in drinking water from 19 wells originating from the shallow aquifer. Characteristics of the wells are shown in Table 1. The locations of the wells were chosen in such a way to represent a range of end uses. The wells that supply water to public buildings, such as schools, kindergartens, shops and restaurants, in densely populated and agricultural areas of middle Podravina were selected. The surroundings of the wells were examined, the sources of pollution were identified, and the distance of the pollution source from the wells was measured by a digital meter (m). The wells were located at a greater or lesser distance from the point sources of pollution of agricultural origin (farms and organic fertilizers depots) and septic systems. Information about the location of septic systems was obtained from the owner of the well, and the distance was measured by a digital meter. During a 6-year study (2002–2007), a total of 253 samples of water were taken during all seasons (2–3 times per year) at the same time (through a week) from each well.

For quality control purposes, duplicate samples were taken and analyzed at a rate of 1 in 20. These were treated as completely separate samples. Precision judged (% RSD) from the duplicates is on average in the range of 2–8 % for nitrate concentration.

The sampling was done according to HRN ISO 5667-5:2000. The water sampling from wells was done after the releasing of water for 2–3 min on the outlet of a water supply system, in a clean polyethylene vessel of 1 l volume. The samples were stored in a portable fridge, in the dark at 1–5 °C for transportation. After delivery to the laboratory, the samples were stored at the same temperature until the analysis (within 24 h).

Water analysis

Nitrate concentration in drinking water was determined using the ion chromatography method (HRN ISO 10304-1:1998). Prior to the injection into the analyzer, ion chromatograph ICS 3000, Dionex (USA), samples were filtered through a membrane filter (of pore 0.45 µm) to remove any particulate matter. After establishing the calibration function, samples were injected into the ion chromatograph and the peaks were measured in accordance with the manufacturer's instructions.

The chromatograph system consists of the following components: auto sampler device, sample injection system (incorporating sample loop of 50 µl), gradient pump, liquid chromatography device, conductivity detector and eluent generator. The AS 15 anion separator column and appropriate precolumn were used for the separation. ASRS ULTRA II-4 mm performed chemical suppression. 38 mM NaOH was used as an eluent, and the flow was 0.5 ml/min.

Table 1 Characteristics of the wells by regions (R1–R6)

Region	Well	Well depth (m)	Pollution source	Proximity (m)	Soil type
R1	W1	6	Ag	>20	Gravel–sand
R1	W3	5	Ag, SS	>20	Gravel–sand
R2	W7	5	Ag	<10	Silt–gravel–sand
R2	W8	6	Ag	>20	Silt–gravel–sand
R2	W18	5	Ag	<10	Silt–gravel–sand
R3	W1	10	Ag	>20	Clay–silt–gravel
R3	W3	5	Ag	>20	Silt–gravel–sand
R3	W4	10	Ag	>20	Clay–silt–gravel
R3	W7	7	Ag, SS	10–20	Clay–silt–gravel
R4	W1	5	Ag	>20	Silt–gravel–sand
R4	W2	5	Ag	>20	Silt–gravel–sand
R4	W9	7	SS	>20	Gravel–sand
R5	W3	10	SS	10–20	Clay–gravel
R5	W4	10	Ag	>20	Clay–gravel
R5	W5	10	SS	10–20	Clay–gravel
R5	W6	15	Ag	<10	Clay–gravel
R6	W1	20	SS	>20	Gravel–sand
R6	W3	10	Ag, SS	<10	Gravel–sand
R6	W5	5	Ag, SS	<10	Clay–gravel

R region, *W* well, *Ag* agriculture, *SS* septic systems

The whole system was supervised by Dionex Chromeleon software.

Data analysis

Descriptive statistics was done for all the data ($N = 253$ samples; $N = 114$ data), and it was compared to the MAV Regulation (2013), i.e., recommended level value (RLV) of Nitrate Directive (Council Directive 1991). Average nitrate concentrations in each of 19 wells through the 6 years were calculated. Data from each year and location are averaged in order to determine the general water quality in a particular well due to nitrate. Box plots of annual nitrate concentration (mg/l) indicating MAV and RLV were log-transformed (ln) to provide a more symmetric (normalized) distribution.

The difference in the nitrate concentration during the years 2002–2007 among regions (R1–R6) was tested with an analysis of variance (ANOVA).

In order to compare the concentrations of nitrate by wells and depending on the distance from the point sources of pollution in the analyzed period, we used the repeated measure analysis of variance. Since we wanted to detect precisely which group differences were statistically significant, we used the Tukey multiple comparison post hoc test (Davis 2002).

In order to confirm the grouping of wells according to the average annual values and distance from the point source pollution, we used k-means clustering.

In order to analyze and present wells in respect of their annual average concentration of nitrate, we did principal component analysis (PCA).

The correlation between the concentrations of nitrate and depth of wells was done as well as the correlation between the concentrations of nitrate and precipitation.

Descriptive statistics and the repeated measure ANOVA were done using the SAS 9.2. PCA was done using the STATISTICA 8.0 (2011), and graphical presentations were done using both statistical packages.

Results

Nitrate concentration in groundwater

Concentration of nitrate ($N = 114$) in the research area of middle Podravina ranged from <0.1 to 367 mg/l in groundwater from shallow wells, and 29.8 % of the samples were above the MAV.

If we analyze the regions (R1–R6), shown in Fig. 1, we see that there is no statistically significant difference in the nitrate concentration during the years 2002–2007 among regions ($F = 1.98$, $p = 0.15$), and the interaction between regions and years is not statistically significant too ($F = 0.99$, $p = 0.49$).

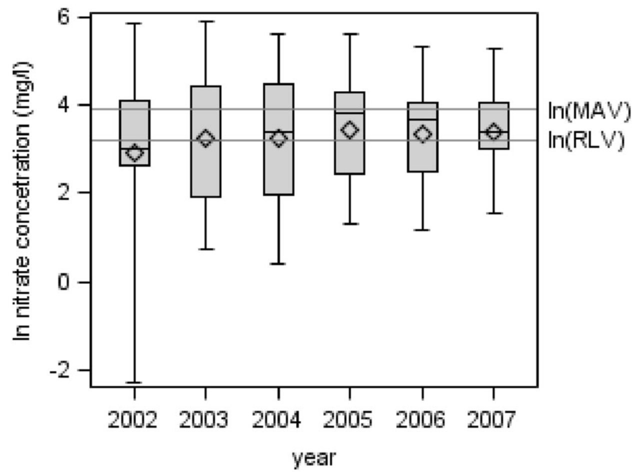

Fig. 2 Box plot of annual nitrate concentration (mg/l) indicating RLV (recommended level) and MAL (maximum allowed level) (*filled circle* mean, *hyphen* median, Q1–Q3 box, min–max whiskers)

The box plot of an annual nitrate concentration (mg/l) indicating MAV and RLV is shown in Fig. 2. Box plots, log-transformed to provide a more symmetric distribution, show that the average concentration of nitrate in all 19 wells for all the analyzed years was between RLV and MAV except in 2002 when the concentration was under the RLV. The distribution of the concentration of nitrate per year (mean, median, min and max) shows that the 2002 distribution was negatively asymmetric which means that most of the wells (over 50 %) had values below the RLV and almost 70 % below the MAV; 2003 and 2004 distribution was symmetric, i.e., about half of the wells had average concentration values up to the RLV. In 2005 and 2006, half of the wells had a concentration higher than the average and higher than the RLV, in 2005 almost reached the maximum (MAV), and after that value slightly decreased until 2007 (half of the wells had the average value that is slightly higher than the RLV). Nitrate pollution is present in wells of all regions, and during a 6-year study, there are year-to-year nitrate concentration differences. Figure 2 also shows that the highest variability of nitrate concentration was established in 2002. It is assumed that extremely low concentrations (detection limit—DL) of one well (R3W1) increase the total variability (negatively asymmetric) in 2002. Considering that the nitrate concentrations in the well are below the RLV and that the well is not exposed to contamination, it is difficult to explain the reason for the variability.

Point sources of nitrate pollution

The results of the repeated measure ANOVA show that there is a statistically significant difference in the concentration of nitrate due to the point source distance (Table 2).

Results of Tukey post hoc tests show that there is statistically significant difference between the wells within 10 m from the point sources of pollution compared to the wells within 20 m from the source of pollution ($F = 10.6$; $p < 0.001$), while the wells within 10–20 m from the point sources are not statistically different from wells within 10 m and within 20 m.

Average values of nitrate during the years are not statistically different, but the interaction between point source distance (proximity) and years is statistically significant ($F = 2.07$; $p = 0.04$), which indicates that the concentration of nitrate during the monitoring does not behave the same with respect to the distance (Fig. 3). Average values of nitrate concentration for wells whose distance is >20 m increase over the years, while those whose distance is <10 m decrease. In the group of the wells at the distance of point sources >20 m, nitrate concentration is generally below the MAV, and only in one well (R4W9), a concentration above the MAV in 2005 (74.2 mg/l) and 2006 (57.5 mg/l) was determined. After that, the concentration in that well decreases again.

Table 2 Results of repeated measure analysis of variance for ln of nitrate concentration

Source of variation	DF	Mean square	*F* value	Pr > *F*
Between subject				
Point source distance	2	46.50	10.58	0.001
Error	16	4.39		
Within subject				
Year	5	0.06	0.23	0.956
Point source * year	10	0.52	2.07	0.036
Error	80	0.25		

Figure 3 also shows that the average concentration of nitrate at the distance of point sources <10 m is the highest in 2003. In a well (R2W7) from this group, concentration ranged from 43.6 to 186 mg/l. The maximum nitrate concentration (186 mg/l) was determined in 2003. In 2004, the concentration decreased (157 mg/l), and a decreasing trend continued until 2007. The variability of the above-mentioned well suggests an average increase in nitrate concentration in 2003. The figure shows that there are differences in the average concentration from year to year and that the variability of individual wells influences the average nitrate concentration through a period of research from 2002 to 2007. The reason behind the variability of the above-mentioned well is unknown.

It is evident that the proximity of point sources of pollution affects the average nitrate concentration. Figure 4 shows the grouping of the wells, considering the type of pollution (of agricultural origin—Ag, septic systems—SS) and a comparison with RLV and MAV. Results of k-means clustering confirmed a division into four clusters according to the pollution. Cluster 1 (R6W3AgSS) is the highest one with an average value ranging from 201 to 367 mg/l during the years and is far higher than the MAV. Cluster 2 (R2W7Ag, R2W8, R2W18Ag, R4W9SS, R5W5SS, R5W6Ag, 6W5AgSS) clustered wells whose average values are over the MAV, and it is evident that this includes

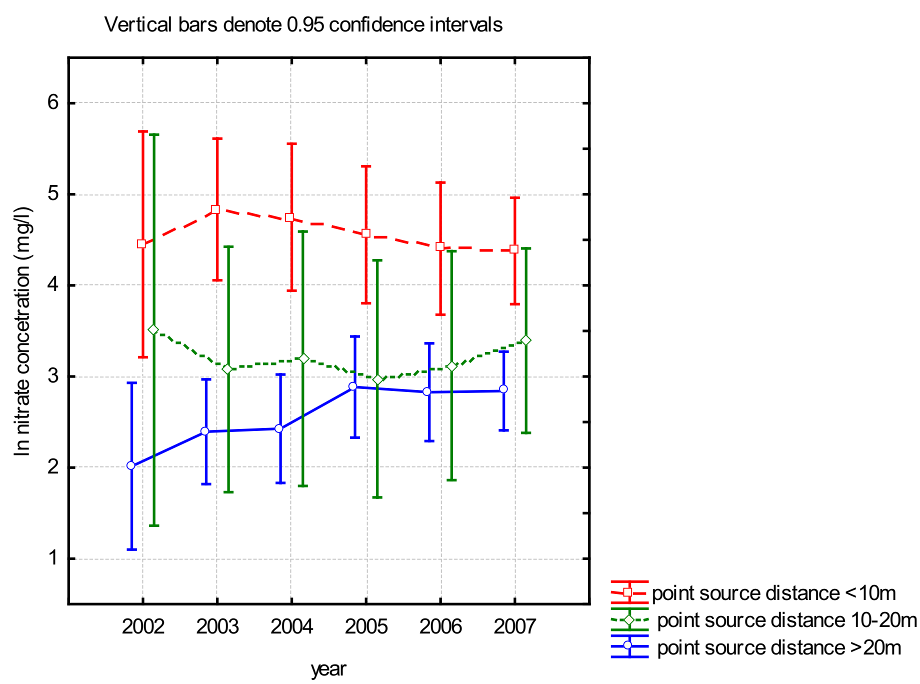

Fig. 3 Average of ln nitrate concentration (mg/l) and 95 % confidence intervals according to point source distance (m)

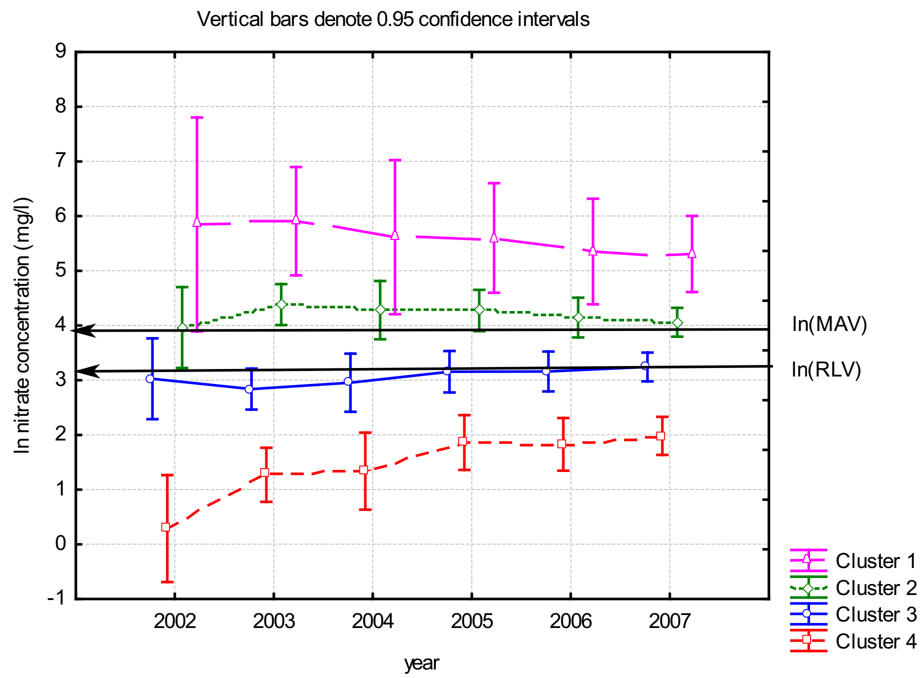

Fig. 4 Average of ln nitrate concentration (mg/l) of 4 clusters according to k-means clustering. RLV (recommend level) and MAL (maximum allowed level)

all wells that are exposed to Ag, SS or both. Cluster 3 (R1W1, R3W3, R3W4, R3W7, R5W3SS, R6W1, R4W1) has the nitrate concentration values a little less than the RLV, while cluster 4 (R1W3, R3W1, R4W2, R5W4) is the lowest.

According to the results, it is clear that the wells that are close to one type of point source of pollution (agriculture or septic systems) show an increased nitrate concentration, while the wells close to both types of pollution are most likely to have nitrate problems.

In the wells far from pollution (Cluster 3 and Cluster 4), established nitrate concentrations are lower (mostly below the RLV). However, according to Fig. 4, it can be seen that the difference in nitrate concentrations was also determined in these wells.

Given that the other environmental factors have not been studied in detail, we determined how many point sources of pollution contribute to the total variability of nitrate in the wells. Principal component analysis projections of the wells with respect to the first two factors according to the average annual nitrate concentration are shown in Fig. 5. Our results show that the first factor explains 91.6 % of the total variability, which means that the distance point source (proximity) is a very important predictor, and another factor accounts only for 5.67 %. We can see that the clusters are lined up one after the other and that the concentration of nitrate following point source distance varies from highest to the left to lowest to the right. The figure also shows that cluster includes two wells away from point sources of >20 m. In these wells, concentrations are close to the MAV (R2W8) or occasionally above the MAV (R4W9SS). Similar characteristics of these wells are such that nitrate concentrations are high even though the distance of point source is large or it is not determined at all.

Effects of multiple factors

The characteristics of the wells are very significant for contamination in shallow wells. For this reason, the correlation between the depth of the wells and nitrate concentrations was examined. There is no statistically significant correlation between the concentrations of nitrate and depth of wells (mean = 8.32 m, SD = 4.08 m) for any observed year ($r2002 = -0.02$, $r2003 = 0.14$, $r2004 = 0.11$, $r2005 = 0.11$, $r2006 = 0.07$, $r2007 = 0.07$).

In addition to depth, several other factors, for example precipitation, may be associated with more frequent contamination problems. The effect of some other factors (precipitation) can be related to the soil characteristics. According to the results, there was no statistically significant correlation ($r = -0.12$) between the average amount of rainfall (mm) per year and the average nitrate concentration.

Discussion

In the region of middle Podravina, a relatively high nitrate concentration (to 367 mg/l) was found in water wells from the shallow aquifer consistent with results of previous research. Kattan (2001) found a concentration of nitrate in

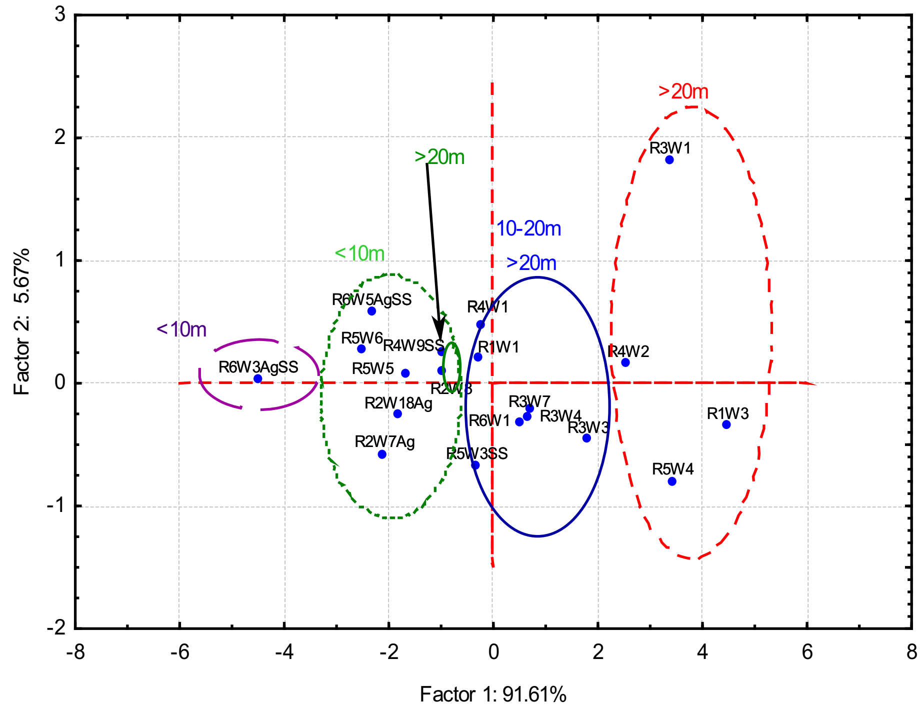

Fig. 5 Projections of the wells with respect to the first two factors (PCA) according to the ln of average annual nitrate concentrations indicating cluster membership and point source distance (Ag—agricultural source, SS—septic systems source, AgSS—both sources)

shallow wells ranging from 11 to 80 mg/l and some other researchers (Obeidat et al. 2007) ranging up to 330 mg/l in the wells, which was recognized as contamination. Other researchers reported an even lower nitrate concentration (8.5 mg/l) in drinking water (Hallberg 1989) that they already considered as pollution, while Kazemi (2004) and Jalali (2005) point out that the concentration of 14 mg/l is satisfactory because it is far below the MAV. Aelion and Conte (2004) found a low concentration (0.94 mg NO_3-N/l) in their research area. However, after an increase in the intensity of use of agricultural land, an increase in nitrate concentration up to 3 mg NO_3-N/l followed. Although scientists have different opinions about the concentrations considered as pollution, it is evident that 29.8 % of samples (above the MAV) in middle Podravina are contaminated by nitrate.

Contaminations of some wells do not necessarily reflect a generalized contamination of local or regional aquifers. Consistent local patterns of contamination probably indicate contamination of the aquifer locally (Richards et al. 1996; Bouwman et al. 2005). It is evident that the nitrate problem exists in all regions, but the nitrate concentration does not depend on the region but on the location of the wells within the region. This difference could be explained as a result of different specific habitat factors (Singh et al. 2015).

Although ammonia and nitrite can cause water quality problems, nitrate is most often associated with the contamination of drinking water (Follett and Hatfield 2001). In the earlier Podravina research, ammonia was not detected in the analyzed samples and it very rarely occurs in waters from shallow wells, whereas nitrate is very often a cause of water contamination. The water from the aquifer in the research area is rich in oxygen, and if ammonia occurs, it probably rapidly oxidizes to nitrate by redox processes (Houben et al. 2001; Follett and Hatfield 2001; Gates et al. 2008).

The most common sources of nitrate contamination include fertilizers, livestock manure, feedlots, septic tanks and land application of municipal sludge (Addiscott et al. 1991; Elhatip et al. 2003; Obeidat et al. 2007). Plant and livestock production in the middle Podravina region is well developed, but the infrastructure (water supply and sewage systems) in settlements that are supplied with water from shallow aquifers, i.e., wells, has not been built yet. Also, point sources of pollution like septic systems can often be found near the wells so these results were expected. Woo-Jung et al. (2007) compared the concentrations of nitrate during 3 years of monitoring in the agricultural area with various sources of pollution, such as sown agricultural land, farms of livestock or dense population, in order to determine types of source contaminations. They found a different variability and in some areas an increase in nitrate concentration above the MAV. In accordance with our results, they determined the lowest concentration of nitrate in the natural area where there are no sources of pollution close to the well, following the crop area. The largest concentrations were found in densely populated areas as well as in the areas with the farms close to the wells. The monitoring of the nitrate concentration in middle Podravina during a 6-year period has also shown that water from the wells far from pollution (determined by surveying of the well surroundings) was not contaminated by nitrate. The contamination by nitrate was determined in densely populated areas in the vicinity of point sources of agricultural origin (leaching from organic waste of private farms) or septic systems. Such results are shown by Krapac et al. (2002) as well, but alongside the type and vicinity of the source of contamination, the type of soil is also important for the leaching of nitrate (Ciravolo et al. 1979). By monitoring groundwater over 8 years, Ciravolo et al. showed contamination from the source of contamination in the area with sandy soil, while they did not determine significant water contamination in the area of clay soil. They emphasize the importance of the distance of point sources of pollution of the wells, but the effect of the impact depends on the permeability and the type of soil. Given that in Podravina there is sandy and gravelly soil (less clay soil), the obtained results are consistent with the hypotheses.

In this study, it was found that when the distance between the point sources and the wells was within 10 m, nitrate concentrations were above the MAV. In contrast, when the distance was greater (more than 10 m), effect on water quality was much rarer. Richards et al. (1996) also showed that the concentration of nitrate is significantly higher in well close to point source (within 6 m) of agricultural origin or septic systems from the well, compared to the concentration far from point source (within 60 m). It is obvious that the distance of the point source contributes to the final concentration of nitrate and nitrate variability. Gardner and Vogel (2005) also pointed out that distance and numbers of septic tanks and point sources of agricultural origin contribute to an increased nitrogen concentration in water even at distances up to 300 m and that the proximity of these types of pollution is a prerequisite for poor water quality due to nitrate.

In the study area, four clusters are shown according to the level of pollution. Water from wells close to point source pollution was worst quality. In wells that are far from point source, water quality is better, but nitrate concentrations are different. Factors that contribute to the difference in the nitrate concentration are not identified in this paper, but are assumed to be the result of the geological structure and porosity of the soil. The physical and chemical weathering of minerals, leaching and runoff are the main factors responsible for groundwater quality deterioration with some geogenic contribution from soil (Singh et al. 2015). The structure and depth of the wells and the proximity of diffuse pollution of agricultural origin or the use of agrochemicals on intensive agricultural areas affect the concentration of nitrate in groundwater in some locations of wells (Elhatip et al. 2003; Burkart and Stoner 2007; Kraft and Stites 2003). This result emphasizes the fact that vulnerability factors bear only a probabilistic relationship to the concentration of contaminants in a well and that even under conditions that combine several factors associated with a low concentration, a certain proportion of wells are contaminated.

Nemčić-Jurec et al. (2007), Melian et al. (1999), Nemčić-Jurec et al. (2013) identified multiple effects of different sources of pollution including agricultural point sources, since their samples had been mostly analyzed in connection with other point sources of pollution. However, some of the previous researches showed the pollution effect of different point sources like septic systems (Drake and Bauder 2005) and agricultural point sources (Widory et al. 2003). In this study, PCA showed that the distance is the main reason for the total variability, which means that it is a very important predictor in middle Podravina. Concentration of nitrate following point source distance ranges from highest (within 10 m, wells are exposed to Ag and SS) to lowest (wells are not exposed to contamination) which is in accordance with above-mentioned studies.

Concentrations of nitrate have shown different trends during the study. A higher nitrate concentration from year to year may be related to lower organic C content in older soils, and consequently less removal of nitrate by reduction or because of older wells, deteriorating structure and higher permeability (Richards et al. 1996). According to the results (data obtained from the Metrological and Hydrological Service) from 2004 to 2007, the annual precipitation is higher (753–991 mm) on average compared to the initial period of the study (740 mm–748 mm), which may contribute to the difference in the concentration of nitrate in the wells, in whose vicinity there are no point sources. However, there is a possibility of influencing underground water through diffuse sources of pollution, which can in general contribute to increasing concentrations in most of the wells. Nitrate concentration changes over time, and the interpretation of research results can be affected by the duration of the research period. Brian et al. (2004) emphasized that geocemical processes are too slow. They showed increase in nitrate concentration in groundwater during 3 years of monitoring. They pointed out that longer period of monitoring includes processes and the influence of potential hazards on groundwater quality. Variability or trends of water quality can be determined by 3 or more years of monitoring. The monitoring of trends during a period longer than 6 years was done by other researchers (Thorburn et al. 2003) reporting 4 categories of trends according to nitrate concentration: varying, steady, decreasing and increasing categories. They showed the effect on water quality during a longer period of time, as well as different effects of point sources near wells and influence of other agroecological factors.

Changes in the soil can affect the transport of nitrate. Alluvial areas which are usually formed by the deposition of soil or sediments have high porosity and permeability. They are considered good for groundwater recharge, and hence, they are also very vulnerable to groundwater pollution in comparison with confined aquifers (Singh et al. 2015). The concentration and variability of nitrate in water depend on the vertical and horizontal transports (Houben et al. 2001). According to Houben et al., vertical transport depends on the distribution of the reactive material in the aquifer, and it is estimated that the velocity of reactive vertical transport of pollutants is on average a few cm/year, whereas nonreactive is much faster, 1 m/year. They found the highest concentrations of nitrate in shallow layers of the aquifer that are richer in oxygen, and transport of nitrate is the fastest. According to Katz et al. (2004), the average concentrations of nitrate were similar in the shallow and deep zones, but the maximum content was much higher in the shallow zone compared to the deep zone. They point out that the concentration of nitrate is highly variable and that the variability of nitrate concentration is greater in shallow layers. As previously mentioned, the variability of nitrate concentrations in Podravina was also recorded in some wells close to pollution.

According to the studies of the Geological Survey, the hydraulic conductivity values range on average between 1×10^{-3} and 3×10^{-3} m/s. The analysis of anisotropy has found that the maximum anisotropy is determined in the shallowest part of the soil (2–7 m depth) made of gravel and sand. In the research area, the anisotropy coefficient usually varies from 10 to 35, while the vertical hydraulic conductivity is 10–35 times smaller than the horizontal. The results showed that the maximum horizontal conductivity is in a 5-m-deep layer (the most common depth of the monitored wells), which further explains the transfer of nitrate from the point source of pollution to the well. The nitrate of agricultural origin was leached for years from point sources into deeper layers, while septic systems are also often several meters deep and are often to be found at the level of the wells. For this reason, contamination of the wells through higher horizontal conductivity of nitrate was expected. Considering that the wells are shallow (mostly 5–10 m depth) and that in the research area, the soil is easily permeable, horizontal hydraulic conductivity values are high and a rapid transfer of nitrate from pollution sources to the well is expected, contributing to variability in individual wells. These shallow wells are more often irregularly, unsafely and spontaneously constructed. We assume that such kind of wells construction contributes to variability of water quality in the wells. Nemcic-Jurec et al. (2013) had examined nitrate concentration in part of Podravina not far away from the study area examined in this paper. Both areas showed similar geological structure and similar average nitrate concentrations (about 25 mg/l). However, proportions of samples above the MAV are different. According to Nemčić-Jurec et al. (2013), only 6 % was above the MAV, while at the nearby area examined in this paper, proportion of samples above MAV was significantly higher, about 30 %. We assume that similar geology and hydrogeology contribute to similar average nitrate concentrations in both areas, while higher proportion of samples above MAV shows periodically higher nitrate concentrations and higher variability. Differences are probably caused by micro-location and by safe environmental conditions, by proximity of source of pollution and by well construction itself. Bad and unsafe well construction and bad environmental conditions like proximity of source of pollution contribute to periodically higher nitrate concentrations, and they are an important prerequisite for poor water quality. Actually, bad and unsafe wells are indicators of proximity of pollution.

The perennial accumulation of nitrate in the soil near the source of pollution contributes to nitrate leaching into groundwater and drinking water in wells (Katz et al. 2004).

Richards et al. (1996) and McLay et al. (2001) have shown that the characteristics of the wells are very important for the contamination of groundwater from shallow wells. In the study area, the wells are usually shallow, and the difference in depths is not significant (90 % of the monitored wells are at 5–10 m depth), it is expected that there is no relationship between nitrate concentration and depth of the wells. Such a relationship should be investigated in different geological areas and in wells with significantly greater differences in depth (range 5–30 m or more). Previous research (Richards et al. 1996; McLay et al. 2001) determined the negative correlation between nitrate concentration and significantly different depth of wells (between wells <15 m deep and wells >30 m deep).

As previously noted, the effect of precipitation on wells depends on the characteristics of the soil and wells in sandy soils more frequently exceed the MAV. The alluvial aquifer is particularly sensitive to pollution (Burkart and Stoner 2007; Singh et al. 2015). Podravina predominantly has alluvial aquifers, but correlation between rainfall and nitrate concentration has not been established. Whatever the exact explanation for the unexpected relationships with well water quality shown by these two factors (precipitation and type of soil), it is clear that if they have any tendency to contribute to an increase in nitrate concentration, this tendency is small enough to be masked by confounding factors acting in the other directions. Similar results were obtained by other researchers (Burkart and Stoner 2007; Kraft and Stites 2003). The largest proportion of wells show varying trends over a longer period of time as a result of all environmental factors, and in these wells, the correlation between nitrate and precipitation was not found. They emphasize that groundwater is particularly sensitive to pollution in areas with a humid climate. More precipitation contributes to the variability of nitrate. However, according to some researchers, one of the more significant environmental factors which influence the concentration of nitrates in wells is precipitation. Pacheco et al. (2001) found the lowest nitrate concentration during the rain season due to dilution of water in wells caused by rain which led to low nitrate concentrations, and they also found a relationship between nitrate and precipitation.

Conclusions

Nitrate-contaminated groundwater has been observed in shallow wells in a typical agricultural region, middle Podravina. Nitrate concentration in some wells exceeded the maximum accepted value of 50 mg/l required by the EU Drinking Water Standards; 29.8 % of the samples were above the MAV.

There is no statistically significant difference in the nitrate concentration during the years 2002–2007 among regions (R1–R6) nor was the interaction between regions and years statistically significant, which indicates that during the monitoring, all regions behaved approximately equally. The nitrate concentration problem was observed in all regions with the key predictor of concentration being the well location within the region.

In the study area, there is a significant difference in the concentration of nitrate due to the point source distance (proximity). Water quality is better in the wells at the proximity of <20 m compared to the wells at the proximity of >10 m. Average values of nitrate during the years are not statistically different. In the wells close to one type of point source pollution (agricultural origin or septic systems), there is an increased nitrate concentration, while in the wells close to both types of contamination, the water is more frequently unsafe for health. Point source distance (proximity) explains 94 % of the total variability of nitrate, which means that the proximity is a very important predictor. Bad and unsafe well construction also contributes to periodically higher nitrate concentrations. It is an indicator of pollution proximity, and it is an important prerequisite for poor water quality.

Because high nitrate concentrations in water can cause different health problems, it is necessary to protect drinking water in the study area. High nitrate concentrations are associated with improperly located wells. It is necessary to locate new wells uphill and least 20 m from feedlots, septic systems, barnyards and chemical storage facilities. Monitoring of nitrate in the tested wells should be continued, and specific rehabilitation measures of wells to end users should be proposed. Wherever possible, it is necessary to build a public water supply system to ensure safe drinking water.

It is also important to manage nonpoint sources of water pollution (fields, lawns) to limit the loss of excess water and plant nutrients and match fertilizer applications to precise crop uptake needs in order to minimize groundwater contamination. Careful fertilizer management can reduce nitrate leaching to groundwater.

These measures will contribute to the implementation of the Nitrate Directive in Croatia and the EU, thus providing pollution control and agricultural product safety.

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